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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Pre-Treatment of Filler with Cationic Ketene Dimer

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Abstract of the Disclosure

A filler for paper or paperboard comprising an inorganic pigment and a cellulose-reactive size, a process for preparing the filler in which the inorganic pigment dispersed in water is treated with a dispersion of the cellulose-reactive size
5 before the filler is added to the dispersion of cellulose fibers in a paper machine, and the use of the treated filler in a process for the manufacture of paper and paperboard in order to maintain the capability of the cellulose fiber and filler mixture to receive sizing independently of the level
10 of filler addition.

The present invention relates to fillers of inorganic particles for use in making paper or paperboard that is sized with a cellulose-reactive size such as a ketene dimer.

Inorganic pigments are widely used as fillers in the paper industry. This use is primarily in printing and writing grades where they improve the optical properties and print quality. They also can reduce overall costs, since most pigments cost less than cellulose pulp. However, because they tend to reduce paper strength, their use tends to be limited to the range between an amount that will produce the needed optical properties, on the one hand, and the amount that will weaken the paper to the point where it may break in the machine under the stresses and strains of a productive rate of processing, on the other hand. Within that range, the papermaker seeks to increase the level of mineral filler to reduce costs while maintaining the maximum commercial productivity of the machine.

Within that range, the amount of filler also depends on the need to provide a proper level of sizing, not only for the end use of the paper but also to prevent an excessive absorption of water on the machine after formation of the web; such an excess of water requires additional drying time

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and reduces productivity. It is well-known, for instance from U.S. Patent 4,799,964, that increased use of fillers reduces the efficiency of conventional cellulose-reactive sizing agents. The difficulty in sizing high filler loadings
5 may be caused by the larger surface-to-volume ratio of the fillers relative to the pulp, and since internal sizes work by increasing the contact angle of the surface to be sized, the addition of more surface area causes an increased demand for sizing agent. This is especially true of cellulose-
10 reactive sizes, which are much more efficient than conventional rosin sizes.

As the level of filler increases, it is more difficult to retain the filler in the web, so the filler retention usually decreases. The above-noted U.S. Patent 4,799,964
15 seeks to increase the beneficial inorganic filler loading by flocculating the filler particles. It also claims a decrease in sizing loss resulting from the flocculation, presumably because flocculation decreases the surface-to-volume ratio of the particles. However, according to the patent, the inter-
20 nal sizing efficiency of ketene dimer size added separately to the slurry, while greater than that used in slurry containing unflocculated filler, was still adversely affected by increased filler loading.

There is therefore a recognized need to facilitate the
25 use of higher levels of inorganic fillers while avoiding the loss in cellulose-reactive sizing efficiency that has been associated with increases in filler content, so that the

filler content is not limited by conventional sizing requirements.

According to the invention, a filler for paper or paperboard comprising an inorganic pigment is characterized in
5 that it consists essentially of from about 97 to about 99.9% by weight of the inorganic pigment, from about 0.025 to about 2.7% by weight of a cellulose-reactive size selected from the group consisting of ketene dimers, alkenyl succinic anhydrides, hydrophobic isocyanates, carbamoyl chlorides, and
10 stearic anhydrides, and preferably from about 0.00625 to about 2.7% by weight of a dispersing agent composition comprising at least 95% by weight of a cationic dispersing agent.

Also according to the invention, a process for preparing a filler for paper or paperboard comprising dispersing an
15 inorganic pigment in water before adding it to a paper machine, is characterized in that from about 25 to about 75% by weight on a dry basis of a cellulose-reactive size is dispersed in water with about 20 to 90% by weight on a dry basis of a cationic dispersing agent to form a treatment
20 dispersion, and particles of the inorganic pigment are contacted with the dispersion in the proportion of 0.1 to 2.0 parts by weight of the sizing solids in the dispersion on a dry basis for each 100 parts by weight of the inorganic particles, preferably from 0.3 to 1.0%.

25 Also according to the invention is the use of the treated filler of the present invention in a process for the manufacture of paper and paperboard.

The composition of the filler according to the invention depends on the composition of the treatment dispersion and relative proportions of the solids in the dispersion and the inorganic particles, and can be calculated by multiplying the
5 level of treatment within the 0.1 to 2.0 range by the proportions of solids on a dry basis in the dispersion.

Naturally occurring pigments like clay or ground limestone may be treated when the pigment is being dispersed conventionally in water, whereas synthetic pigments like precipitated calcium carbonate may be treated either during or
10 after conventional precipitation.

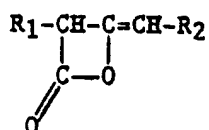
After treatment the dispersed filler of the present invention is stable for subsequent storage and is ready for shipping. The treated filler can be added to the paper stock
15 dispersion any time prior to sheet formation in the conventional process for the manufacture of paper and paperboard, in which a wet laid cellulosic sheet is formed by dewatering the dispersion of cellulosic fibers and then dried to form the paper and paperboard product. Since the treatment
20 renders the filler cationic the retention system may need to be changed, but experience has not shown any dramatic difference in either filler retention or size retention with the use of the treated filler.

Surprisingly, it has been found that the addition of the
25 filler of the present invention avoids the expected loss in cellulose-reactive sizing efficiency, so that the amount of

filler is not limited by the conventionally required levels of sizing.

Preferably, the inorganic pigment filler is conventional particulate material selected from the group consisting of calcium carbonate, clay, titanium dioxide, talc and hydrated silica clay, more preferably calcium carbonate, kaolin clay or titanium dioxide, and most preferably particles of precipitated calcium carbonate. Preferred cellulose-reactive sizes are ketene dimers having the general formula:

10



where R_1 and R_2 are hydrocarbon groups having from 8 to 30 carbon atoms. More preferred are cellulose reactive sizes selected from the group consisting of ketene dimers wherein the R_1 and R_2 groups are selected from saturated and monounsaturated hydrocarbon groups having from 12 to 22 carbon atoms, and alkenyl succinic anhydrides wherein the alkenyl group has from 12 to 30 carbon atoms.

20 Most preferably the cellulose reactive size is a ketene dimer in which the R_1 and R_2 groups are saturated hydrocarbon groups having from 14 to 16 carbon atoms, such as the cationic ketene dimer available as an aqueous dispersion from Hercules Incorporated under the trade mark Hercon^R and
25 trade designations 40, 48 or 85, and 70.

The preferred composition of the dispersion made by the process according to the invention is from 35 to 55% by weight of ketene dimer on a dry basis.

The preferred cationic dispersing agents are naturally occurring cationic polymers (preferably starch), synthetically produced cationic polymers (preferably a polyamine resin), or combinations of both types. The amount required to disperse the solids is determined according to conventional criteria.

10 If the naturally-occurring cationic polymer is used alone, the amount preferably varies from 10 to 35% by weight of the dispersions, and the level of synthetic cationic polymer when used alone ranges from 10 to 75% by weight of the dispersions, both on a dry basis. When the two types are
15 use together, the total amount is preferably at least 10%, with the natural polymer being from about 9 to 20% by weight and the synthetic polymer being up to about 70% by weight of the dispersions, again on a dry basis. A combination of both types is preferred, with the weight ratio of cationic
20 synthetic polymers to cationic natural polymers in the dispersing agent at least 2 to 1.

Preferably, the cationic dispersing agent is selected from the group consisting of cationic starches, cationic gums, cationic polyamines, cationic polyamides, cationic
25 polyurylenes and mixtures thereof, most preferably, it is a cationic starch, a cationic polyamide, or a mixture of both.

While the above mentioned cellulose reactive sizes are

all suitable for use in the present invention, some of the specific description to follow will be in terms of the preferred ketene dimer.

Preferably, the cationic dispersing agent is selected
5 from the group consisting of cationic starches, cationic gums, cationic polyamines, cationic polyamides, cationic polyurylenes and mixtures thereof.

Preferably, the weight ratio of cationic synthetic polymers to cationic natural polymers in the dispersing agent
10 is at least about 2 to 1.

The composition of the filler after the treatment according to the invention, within the above-mentioned limits, depends on the composition of the dispersion used in the treatment. Preferably, the filler contains from about 98
15 to about 99.8% by weight, and most preferably from 99 to 99.7% by weight of the inorganic pigment, and contains 0.1 to 1.8% by weight, more preferably from 0.15 to 0.9% by weight, of the cellulose reactive size. Also more preferably the filler contains from 0.025 to 1.8% by weight, and most
20 preferably from 0.0375 to 0.9% by weight, of the dispersing agent.

Since the cationic dispersing agent need not constitute 100% of the dispersing agent composition, the remaining portion of up to 5% may be an anionic or nonionic dispersing
25 agent.

In the following Examples, handsheets were prepared on a Noble and Wood handsheet machine using a 50% hardwood: 50%

softwood kraft pulp furnish beaten to 500 Canadian Standard Freeness in water containing 100 ppm. hardness and 150 ppm. alkalinity, both expressed as calcium carbonate. The pulp was diluted to 0.25% consistency in the proportioner. The
5 pulp was then diluted further in the deckle box to 0.025% consistency and then the sheet was formed at pH of about 7.5-8.5. Hercon^R 48 was then added to the aliquot taken from the proportioner just prior to dilution of the pulp in the deckle box. The dispersion was added in an amount suffi-
10 cient to provide about 0.20% of the sizing composition based on the dry weight of the pulp. A closed white water system was used. Formed sheets were wet pressed to 33% solids and then dried at 240°F. on a steam heated drum drier for about 45 seconds. The first four sheets of paper prepared were
15 discarded and the next five were tested for sizing properties. The test results set forth in the Tables were the average of five sheets tested. The handsheets were 40 lb./3000 ft.² basis weight.

The sizing was measured by the Hercules Size Test (HST)
20 with test solution No. 2 to 80% reflectance. The off-the-machine data (OM) were obtained within three minutes after drying and natural aged (NA) data were obtained after 7 days storage at 72°F. and 50% relative humidity.

In the following examples, all parts and percentages are
25 by weight unless otherwise indicated.

Examples 1 and 2 and Comparative Examples C-1 to C-5

Filler treatment procedure:

Klondyke clay was diluted to 20% solids in water and was dispersed in a Waring blender on high speed in a plastic container. Dispersant A or Dispersion A, as indicated in the Table, was then added and agitation continued for 2 minutes. The slurries were either used immediately or were reagitated prior to addition to the size crock.

The results obtained after handsheet preparation are summarized in Table I. All ingredients are expressed as solids, based upon the weight of paper.

TABLE I

Example No.	% Clay Added	% Ash	Filler Treatment	HST. sec.	
				OM	NA
15	C-1	0	0.3	---	---
	C-2	10	8.3	---	---
	C-3	20	16.3	---	---
	C-4	10	8.3	Dispersant A(1)	137 175
	C-5	20	16.7	Dispersant A	4 5
20	Ex. 1	10	8.2	Dispersion A(2)	230 275
	Ex. 2	20	16.3	Dispersion A	24 27
(1) Polyamino/polyamide cationic thermosetting resin.					
(2) A cationic KD dispersion containing 36% by weight of solids of a mixed ketene dimer which is prepared from 55% by weight of palmitic acid and 45% by weight of stearic acid and wherein the cationic dispersing agent is Dispersant A.					
25					

These examples show that treatment of clay filler provides improved sizing over the control (no treatment) and

over a cationic resin treatment (Dispersant A). Two levels of filler were added, 10% and 20% which are typical ranges often used in commerce. Comparison of the first three runs shows the normal effect of filler addition; namely, the

5 sizing decreases dramatically from 469 sec. penetration resistance to 3 seconds. Treatment of the filler with cationic resin shows only a very marginal increase over the untreated controls. In contrast cationic KD treated runs gave dramatically better sizing at both the 10% and 20% levels of filler

10 addition.

Examples 3 and 4 and Comparative Examples C-6 to C-8

Filler treatment followed the procedure described in Examples 1 and 2. The results obtained after handsheet preparation are summarized in Table II.

15

TABLE II

Example No.	Filler Added	Filler Treatment	HST, sec. NA	Opacity	% Ash
C-6	None	--	400	74.5	0.35
C-7	10	--	75	84.4	5.11
C-8	20	--	3	88.1	9.83
Ex. 3	10	Dispersion B(2)	116	84.1	5.29
25 Ex. 4	20	Dispersion B	16	88.0	9.29

(1) Precipitated CaCO_3 made by Pfizer Inc. having an average particle size of about 0.73 μ .

(2) A cationic KD dispersion containing 47% by weight of solids of a mixed ketene dimer which is prepared from 55% by weight of palmitic acid and 45% by weight of stearic acid and wherein the cationic dispersing agent is a cationic waxy maize corn starch with a nitrogen content of greater than 0.2%.

30

This example demonstrates the improved sizing effect

obtained by treating precipitated CaCO_3 filler with cationic KD dispersion. Comparing the untreated filler runs, one can see the usual loss in sizing as the filler level is increased.

- 5 The ash and opacity data show that there is no effect of the filler treatment on either of these properties. This implies that both the overall ash retention as well as the optical efficiency of the filler is unchanged.

DESCRIPTION OF KALAMAZOO LAB FORMER (KLF)

- 10 The KLF is a miniature paper machine designed to simulate a commercial Fourdrinier, including stock preparation, refining and storage. A 70% Weyerhaeuser Bleached Kraft/30% Rayonier Bleached Kraft pulp is dispersed in standard hard water as described in Example 1. The pulp
15 is refined at 2.5% consistency in a double disc refiner by recirculation to a freeness of 500 CSF. The stock is then pumped to a machine chest where it is diluted with fresh water to approximately 1.0% solids.

- The stock is fed by gravity from the machine chest to a
20 constant-level stock tank. From here the stock is pumped to a series of in-line mixers (mix boxes - "MB") where wet end additives are added. There are 4 mixing (additive) stations, each with its own in-line mixer. The filler is added first, to mix box #1. It is followed by cationic potato starch,
25 Stalok^R 400, made by Staley, Inc., added to the 2nd mix box at 0.75% dry basis. The internal size, is added to the third

mix box as indicated in the individual examples. Finally, an anionic polyacrylamide retention aid, Reten^R 523, made by Hercules Incorporated, is added to the 4th mixing station at 0.0375%. After passing through the mix boxes, the stock
5 enters the fan pump where it is diluted with white water to about 0.2% solids.

The stock is pumped from the fan pump to a flow spreader and then to the slice, where it is deposited onto the 12-inch wide Fourdrinier wire. Immediately after its deposition on
10 the wire, the sheet is vacuum dewatered via two vacuum boxes; couch consistency is normally 14 to 15%.

The wet sheet is transferred from the couch to a motor driven wet pickup felt. At this point, water is removed from the sheet and the felt by vacuum uhle boxes operated from a
15 vacuum pump. The sheet is further dewatered in a single felted press and leaves the press section at 38 to 40% solids.

The dryer section is comprised of seven steel drum dryers. Both top and bottom sections are felted. The temperatures of the dryers can be independently varied from
20 100 to 240°F. The sheet is dried to 3 to 5% moisture content at the reel.

EXAMPLES 5 TO 10 AND COMPARATIVE EXAMPLES C-9 TO C-11

Filler Treatment:

Filler was dispersed at 15% solids 24 hours prior to
25 papermaking. The treatment is added to the filler on the same day as papermaking, using a Lightning mixer to agitate

the dispersion. Agitation was continued for 5 minutes after treating the filler. The level of treatment is described in the individual examples to follow.

Paper sheets were made on the KLF following the
5 procedure described above. As the internal size all runs contain 0.08% by weight of solids of Hercon^R 70, a cationic ketene dimer dispersion available commercially from Hercules Incorporated.

Filler and treatment levels, and the results obtained
10 are summarized in Table III.

TABLE III

Example No.	Albacar 5970 (1) Filler Added	Filler Treatment	HST, sec.
			NA
5	C-9	10	
	C-10	20	174
	C-11	30	28
			7
	Ex. 5	10	
	Ex. 6	20	0.23% Dispersion C(2) 226
10	Ex. 7	30	0.23% Dispersion C 172
			0.23% Dispersion C 109
	Ex. 8	10	
	Ex. 9	20	0.46% Dispersion C 257
	Ex. 10	30	0.46% Dispersion C 265
			0.46% Dispersion C 283
15	(1) Precipitated CaCO ₃ made by Pfizer Inc. having an average particle size of about 2 m.		
	(2) A cationic KD dispersion containing 45% by weight of solids of a mixed ketene dimer which is prepared from 55% by weight of palmitic acid and 45% by weight of stearic acid and wherein the cationic dispersion agent is a polyamine resin.		
20			

These examples show the importance of treating the filler at high filler loadings. The untreated filler shows the usual loss in sizing. The treated fillers show essentially no loss even though the filler level is increased threefold from 10 to 30%. As the level of filler treatment is increased, the sizing actually can increase as the filler level increases.

EXAMPLES 11 TO 19 AND COMPARATIVE EXAMPLES C-12 TO C-14

Paper sheets were made on the KLF following the procedure described above. As the internal size all runs contain 0.11% by weight of solids of Hercon^R 70, a cationic ketene dimer dispersion available commercially from Hercules Incorporated.

Filler and treatment levels and the results obtained are summarized in Table IV.

TABLE IV

5	<u>Example No.</u>	<u>% Albacar 5970 Filler Added</u>	<u>Filler Treatment</u>	<u>HST, sec. NA</u>
	C-12	10		
	C-13	20	--	210
	C-14	30	--	154
			--	27
10	Ex. 11	10	0.23% Dispersion B	219
	Ex. 12	20	0.23% Dispersion B	284
	Ex. 13	30	0.23% Dispersion B	203
	Ex. 14	10	0.46% Dispersion B	238
	Ex. 15	20	0.46% Dispersion B	361
15	Ex. 16	30	0.46% Dispersion B	338
	Ex. 17	10	0.69% Dispersion B	203
	Ex. 18	20	0.69% Dispersion B	480
	Ex. 19	30	0.69% Dispersion B	426

These examples show the same effect as shown in Examples 20 5 to 10, except obtained at a higher internal sizing level.

EXAMPLES 20 AND 21 AND COMPARATIVE EXAMPLE C-15

Paper sheets were made on the KLF following the procedure described above. As the internal size all runs contain 0.08% by weight of solids of alkenyl succinic anhydride (ASA) dispersed with 0.16% by weight of solids Stalok 400 cationic starch at 2000 psi at room temperature. The dispersion was kept at 20°C prior to use and was used within 3 hours of its preparation. The ASA was Fibran^R 70, available from National Starch Co.

Filler and treatment levels and the results obtained are summarized in Table V.

TABLE V

5	Example No.	% Albacar 5970 Filler Added	Filler Treatment	HST, sec.
				NA
	C-15	20	--	1
	Ex. 20	20	0.08% Dispersion B	110
	Ex. 21	20	0.05% Dispersion C(1)	41
10	(1) Dispersion C is a cationic KD dispersion containing 74% by weight of solids of a mixed KD which is prepared from 55% by weight of palmitic acid and 45% by weight of stearic acid and wherein the cationic dispersing agent is a cationic waxy maize cornstarch with a nitrogen content of greater than 0.2%.			
15	These examples show that both types of cationically dispersed KD dispersions give greatly improved sizing when used with ASA as the internal size.			

EXAMPLES 22 AND 23 AND COMPARATIVE EXAMPLE C-16

20 Paper sheets were made on the KLF following the procedure described above. The runs were internally sized as in Examples 5 to 10.

Filler and treatment levels and the results obtained are summarized in Table VI.

TABLE VI

25	Example No.	% Albacar 5970 Filler Added	Filler Treatment	HST, sec.
				NA
	C-16	20	--	53
30	Ex. 22	20	0.6% ASA(1)	112
	Ex. 23	20	1.2% ASA	277

(1) ASA dispersion described as the internal size in Examples 20 and 21.

These examples show the improvement obtained when the filler is treated with ASA.

EXAMPLE 24 AND COMPARATIVE EXAMPLES C-17 AND C-18

Paper sheets were made on the KLF following the
5 procedure described above. All runs were internally sized as in Examples 5 to 10.

Filler and treatment levels and the results obtained are summarized in Table VII.

TABLE VII

Example No.	Z Albacar 5970 Filler Added	Filler Treatment	HST, sec.
			NA
C-17	20	--	53
C-18	20	0.4% Nalco 7541(1)	46
15 Ex. 24	20	0.4% Dispersion B	416

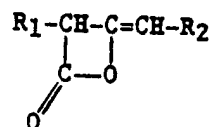
(1) A cationic polyamine resin, commercially available from Nalco Chemicals, made from dimethyl amine and epichlorohydrin.

This example shows that the cationic polyamine resin
20 treatment of the filler did not result in any improvement in sizing. On the other hand, treatment of the filler with the cationic KD dispersion resulted in a significant improvement in sizing.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A filler for paper or paperboard comprising an inorganic pigment, characterized in that it consists essentially of from about 97 to about 99.9% by weight of the inorganic pigment, from about 0.025 to about 2.7% by weight of a
5 cellulose-reactive size selected from the group consisting of ketene dimers, alkenyl succinic anhydrides, hydrophobic isocyanates, carbamoyl chlorides, and stearic anhydrides.
2. A filler as claimed in claim 1, further characterized in that it contains 0.00625 to about 2.7% by weight of a
10 dispersing agent composition comprising at least 95% by weight of a cationic dispersing agent.
3. A filler as claimed in claim 1 or 2, further characterized in that the inorganic pigment comprises particulate material selected from the group consisting of calcium
15 carbonate, clay, titanium dioxide, talc and hydrated silica clay.
4. A filler as claimed in claim 3, further characterized in that the inorganic pigment comprises precipitated calcium carbonate.

5. A filler as claimed in any one of the preceding claims, further characterized in that the cellulose-reactive size is a ketene dimer having the general formula:



in which R_1 and R_2 are hydrocarbon groups having from 8 to 30 carbon atoms, or an alkenyl succinic anhydride in which the alkenyl group has from 12 to 30 carbon atoms.

6. A filler as claimed in claim 5, further characterized in that the cellulose-reactive size is a ketene dimer in which the R_1 and R_2 groups are saturated hydrocarbon groups having from 14 to 16 carbon atoms.

7. A filler as claimed in any one of the preceding claims, further characterized in that the reactive cellulose size is present in an amount of from about 0.1 to about 1.8% by weight.

8. A filler as claimed in any one of the preceding claims, further characterized in that the cationic dispersing are selected from the group consisting of naturally occurring cationic polymers, synthetically produced cationic polymers, or a combination of both types.

9. A filler as claimed in claim 7, further characterized in that the cationic dispersing agent is a cationic starch, a cationic gum, a cationic polyamine, a cationic polyamide, a cationic polyurylene, or a mixture of any of
5 them.

10. A filler as claimed in claim 9, further characterized in that the cationic dispersing agent is a combination of a cationic polyamide and a cationic starch in a weight ratio of at least 2 to 1.

10 11. A filler as claimed in any one of the preceding claims, further characterized in that the cationic dispersing agent is present in an amount of from about 0.025 to about 1.8% by weight.

12. A process for preparing a filler as claimed in any
15 one of the preceding claims for paper or paperboard, comprising dispersing an inorganic pigment in water before adding it to a paper machine, characterized in that from about 25 to about 75% by weight on a dry basis of a cellulose-reactive size is dispersed in water with about 20 to 90% by
20 weight on a dry basis of a cationic dispersing agent to form a treatment dispersion, and particles of the inorganic pigment are contacted with the dispersion in the proportion of 0.1 to 2.0 parts by weight of the sizing solids in the dispersion on a dry basis for each 100 parts by weight of the
25 inorganic particles.

13. A process as claimed in claim 11, further characterized in that and particles of the inorganic pigment are contacted with the dispersion in the proportion of 0.3 to 1.0 parts by weight of the sizing solids in the dispersion on a dry basis for each 100 parts by weight of the inorganic particles.

14. A process as claimed in claim 11 or 12, further characterized in that the cationic dispersing agent is a naturally-occurring cationic polymer in an amount of from 10 to 35% by weight of the dispersion, or a synthetic cationic polymer in an amount of from 10 to 75% by weight of the dispersion, or a combination of both types in a total amount of at least 10%, with the natural polymer being from about 9 to 20% by weight and the synthetic polymer being up to about 70% by weight of the dispersion, all on a dry basis.

15. Use of the filler claimed in any one of claims 1 to 10 in a process for the manufacture of paper and paperboard, in which a wet laid cellulosic sheet is formed by dewatering a dispersion of cellulosic fibers and then dried to form the paper or paperboard product, by adding a dispersion of the filler to the dispersion of cellulose fibers.